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E. I. Klabunovskii, Academician A. A. Balandin,

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chemical structures I and II

Figure 1: chemical structures I and II

Abstract

Full Text

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E. I. Klabunovskii, Academician A. A. Balandin,
R. Yu. Mamedzade

On a Stereochemical Approach to the Study of the Geometry of the Active Surface of Catalysts

It was shown earlier (1) that molecules with a rigid spatial configuration (derivatives of triptycene) are hydrogenated at a noticeable rate on skeletal Ni under comparatively mild conditions.

To explain this fact, it is necessary to assume the presence on the catalyst surface of protruding active centers, on which the index group of the reacting molecule is superposed. Otherwise the reaction would be hindered. The following speaks in favor of such an assumption.

According to the multiplet theory, because of the small radius of action of valence-chemical forces, molecules come into contact with the catalyst surface by their reacting atoms, and this determines the orientation of the molecule during catalysis.

In the reacting molecule the index group (in the case of type I compounds, the double $C_{11} = C_{16}$ bond) is located in the "depth" of the molecule, whose structure does not permit contact with the catalyst in the absence of protruding centers on its surface.

The molecule has a rigid spatial structure that excludes S_N2- or S_N1-mechanisms.

The invariance of configuration in reactions can probably also be demonstrated by preservation of optical activity during catalytic transformations of atropisomeric bicyclic compounds (2,3). If the index group is located "in the depth" of the molecule, increasing the complexity of the rigid carbon skeleton of the bridging substituents should lead to a slowing of the reaction, for example for II in comparison with I, as is shown in the experimental part of the present work. If, however, the index group is not located "in the depth" of the molecule, as in the hydrogenation of adduct III, and possibly also IV, then increasing the complexity of the aromatic part of the molecule should not substantially affect the rates of hydrogenation.

chemical structures III–VIII

Figure 2: chemical structures III–VIII

Hydrogenation of quinones V–VIII, which have a structure analogous to III and IV, proceeds by a different mechanism; however, here too no substantial influence is observed of the structure of the hydrocarbon part of the molecule on the hydrogenation rate constant, which is significantly affected only by linear annelation in the quinonoid system (4). This is also confirmed by comparison of the values of the half-wave potentials in polarographic reduction of the indicated quinones (5), as well as by the stability values of the semiquinones ($E^{I}_{1/2} - E^{II}_{1/2}$), with a linear dependence existing between the value $\lg K$ and ($E^{I}_{1/2} - E^{II}_{1/2}$):

$$\lg K = A(E^{I}_{1/2} - E^{II}_{1/2}).$$

When considering the data on the hydrogenation of I, II, on the one hand, and III, IV and V–VIII, on the other, it is necessary to bear in mind the different reaction mechanisms; therefore these data must be compared with caution. With considerable justification one could compare the hydrogenation of I, II with III. For compounds with a large redox potential (quinones, some aromatic hydrocarbons (6)), hydrogenation proceeds through the formation of an intermediate ionic form.

In the case of the reaction of molecules with a rigid skeleton on the catalyst surface, there must exist a set of optimal centers that provide the best structural correspondence with the reacting molecule.

If steric hindrances are small, then even in the case of bicyclo-(2,2,2)-compounds the reaction may proceed readily, as, for example, in the hydrogenation of barrelene on PtO_2 in ethanol (7). A change in the character of active centers having optimal geometry, both toward an increase in their parameters and their number and toward "leveling" of the surface, will lead to a decrease in the rate of reaction I (or II), since the probability of finding such optimal active centers on the catalyst surface will decrease.

However, a decrease in the rate of hydrogenation by itself may indicate only a reduction in the number of such optimal active centers. The question of the character of the active surface of the catalyst can be resolved by selecting reacting molecules of a definite structure and carrying out reactions on one catalyst, or by studying reactions of one compound using different catalysts.

In addition, investigation of the mechanism of hydrogenolysis proceeding by an S_N1, S_N2, or S_{Ni} type, in the case of optically active benzyl-type compounds, may provide information on the greater or lesser "microroughness" of the catalyst surface (8). Recently the hydrogenolysis of a large number of optically active atrolactates and other compounds on Ni has been studied. From these data it may be concluded that the surface of Ni catalysts is more "microrough" than

Fig. 1. Planar arrangement of the model of molecule II on the active center of the surface of a nickel catalyst

Figure 3: Fig. 1. Planar arrangement of the model of molecule II on the active center of the surface of a nickel catalyst

that of Pd catalysts, since in the first case a nonspecific mechanism of the S_N1 type predominates, involving removal of the asymmetric carbon atom from the surface, whereas in the second case the reaction proceeds to a significant extent stereospecifically—with retention or inversion of configuration according to S_{Ni} or S_N2 mechanisms (9).

As follows from these data, the distances between the active centers of the Ni catalyst are no more than 10 Å. The dimensions of molecule I are 11.0 Å, and in the case of II, 12.0 Å. Such proximity of the active centers will naturally hinder the course of the reaction. Moreover, as follows from the model in Fig. 1, made to scale, adsorption and catalysis of molecule I (or II) require a special configuration of the active center (10). The dimensions of the model of molecule II were obtained with allowance for a certain decrease, according to (11), of the angle a, taken as equal to 25°.

In the present work, the hydrogenation of I and II was investigated, and, for comparison, the hydrogenation of diethyl maleate on skeletal Ni and Pd/C catalysts was also studied. To assess the effect of the degree of dilution of the catalyst on the support, 1 and 10% Pd on carbon were used.

The reaction was carried out in a medium of dioxane and dimethylformamide (DMF) at 45° and atmospheric pressure. The preparation of the initial compounds, their constants, and the preparation of the catalysts have been described earlier.

In Table 1 and in Fig. 2 are given the experimental conditions and the data obtained. For each substance on three catalysts the first-order rate constants (K) with respect to the substance being hydrogenated and the ratio of the rate constant to unit weight of catalyst (K/n)—the "specific activity"—are indicated. As is evident from the data of Table 1, the rates of hydrogenation in DMF are greater than in dioxane. In the latter solvent, diethyl maleate is hydrogenated on Ni and Pd/C with close values of K/n. Comparison of the hydrogenation of I and diethyl maleate on Ni shows that I is hydrogenated 10 times more slowly, and II 3 times more slowly than I (it should be borne in mind that the comparative hydrogenation of I and II was carried out on catalysts of different activity than the comparative hydrogenation of diethyl maleate and I).

Fig. 1. Planar arrangement of the model of molecule II on the active center of the surface of a nickel catalyst

On Pd/C catalysts, II is likewise hydrogenated 2-4 times more slowly than I, while the latter is hydrogenated 10 times faster in DMF and 1.5-2 times faster

Fig. 2. Kinetic curves for the hydrogenation of I and II in dimethylformamide. 0.15 g Ni: 1 —1.2 mmole I; 2 —1.2 mmole I; 0.015 g Pd (10% Pd/C); 3 —0.5 mmole I; 4 —0.5 mmole II 0.015 g Pd (1% Pd/C); 5 —0.5 mmole I; 6 —0.5 mmole II

Figure 4: Fig. 2. Kinetic curves for the hydrogenation of I and II in dimethylformamide. 0.15 g Ni: 1 —1.2 mmole I; 2 —1.2 mmole I; 0.015 g Pd (10% Pd/C); 3 —0.5 mmole I; 4 —0.5 mmole II 0.015 g Pd (1% Pd/C); 5 —0.5 mmole I; 6 —0.5 mmole II

in dioxane than diethyl maleate. Attention is drawn to the fact that, despite its complex spatial configuration, on 10% Pd/C I is hydrogenated almost 10 times faster than diethyl maleate. Here the strong influence of adsorption of nonindexed substituents on the free surface of the support—carbon—is manifested.

Fig. 2. Kinetic curves for the hydrogenation of I and II in dimethylformamide. 0.15 g Ni: 1 —1.2 mmole I; 2 —1.2 mmole I; 0.015 g Pd (10% Pd/C); 3 —0.5 mmole I; 4 —0.5 mmole II 0.015 g Pd (1% Pd/C); 5 —0.5 mmole I; 6 —0.5 mmole II

Comparison of the values K/n for hydrogenation on Ni, 10% Pd/C, and 1% Pd/C shows that for the ester they are in the ratio $1 : 2.8 : 1.6$ (in dioxane) and are practically the same, whereas for I (in dioxane and DMF) they are $1 : 22\text{-}43 : 15\text{-}31$, and for II this ratio is $1 : 18 : 22$. The results obtained can be considered in light of the views expressed above. Indeed, the ratio of the hydrogenation rates of I and II on Ni, 10% Pd/C, and 1% Pd/C catalysts is almost the same, while on Pd/C catalysts both of these compounds are hydrogenated (comparing the values K/n) 15-20 times better than on Ni.

Table 1

Hydrogenation of diethyl maleate, 12,13,14,15-tetrahydro-12,15-dioxo-(9′,10′-dihydroanthrylene-9′,10′)-tripticene (I), and 12,13,14,15-tetrahydro-12,15-dioxo-2,3:6,7-dibenzo-(9′,10′-dihydroanthrylene-9′,10′)-tripticene (II) on skeletal nickel and palladium on carbon at 45° and atmospheric pressure

Hydrogenated compound	Ni, $K \cdot 10^2$	Ni, K/n	10% Pd/C, $K \cdot 10^2$	10% Pd/C, K/n	1% Pd/C, $K \cdot 10^2$	1% Pd/C, K/n	Amounts of catalyst, hydrogenated substance, solvent
$\mathrm{CH{-}COOC_2H_5}$ ‖ $\mathrm{CH\ COOC_2H_5}$	16.1	0.21	8.8	0.59	0.50	0.33	0.75 g Ni0.15 g 10% Pd/C0.15 g 1% Pd/C2 mM dioxane, 50 ml
[[structural formula of compound I, anthracene-quinone tripticene skeleton]]	1.54	0.02	12.52	0.83	1.08	0.72	
$\mathrm{CH{-}COOC_2H_5}$ ‖ $\mathrm{CH\ COOC_2H_5}$	3.12	0.42	2.55	0.17			0.75 Ni0.15 10% Pd/C0.015 1% Pd/C2 mM

Hydrogenated compound	Ni, $K \cdot 10^2$	Ni, K/n	10% Pd/C, $K \cdot 10^2$	10% Pd/C, K/n	1% Pd/C, $K \cdot 10^2$	1% Pd/C, K/n	Amounts of catalyst, hydrogenated substance, solvent
[[structural formula of compound I, anthracenequinone tripticene skeleton]]	2.65	0.04	26.00	1.73			dimethylformamide50 ml
[[structural formula of compound II, dibenzo anthracenequinone tripticene skeleton]]	2.38	0.16	5.34	3.56	3.54	3.26	0.15 Ni*; 1.2 mM0.015 g 10% Pd/C0.015 1% Pd/C0.5 mM

Hydrogenated compound	Ni, $K \cdot 10^2$	Ni, K/n	10% Pd/C, $K \cdot 10^2$	10% Pd/C, K/n	1% Pd/C, $K \cdot 10^2$	1% Pd/C, K/n	Amounts of catalyst, hydrogenated substance, solvent
[[structural formula of compound II, extended dibenzo anthracenequinone tripticene skeleton]]	0.76	0.05	1.32	0.88	1.66	1.11	dimethylformamide50 ml

* The catalysts in this series of experiments had a different activity.

At the same time, the hydrogenation of II proceeds on Ni and Pd/C catalysts 2–4 times more slowly than the hydrogenation of I. This is explained by catalytic hindrance, since in molecule II there is a pentacene residue on the side of the $C_{11} = C_{16}$ double bond. This thereby confirms the assumptions made above regarding the substantial role of steric hindrance in catalysis.

Institute of Organic Chemistry
named after N. D. Zelinsky
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.